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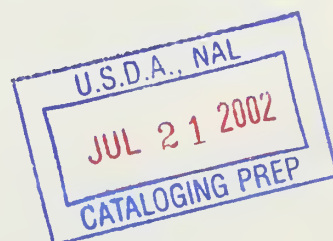
FINAL REPORT

A STUDY OF THE EFFECTS OF INCREASED UV-B IRRADIATION ON
ENVIRONMENTAL DISSIPATION OF AGRICULTURAL CHEMICALS

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Introduction

Many synthetic compounds have been introduced into the biosphere
through human activities. Agricultural chemicals are widely dissipated
in the environment and exposed to many natural processes. Sunlight is
an extremely effective natural force in degrading or destroying many
synthetic chemicals and phenomena such as bleaching, fading of dye-
stuffs, and drying of paints are examples. Inorganic compounds are
generally quite resistant to the action of sunlight.

Many fertilizers and some of the older inorganic pesticides may
be included among resistant chemicals. However, the large-scale pro-
duction of synthetic organic compounds has changed the situation to a
considerable degree. Since the 1940's, there has been continuous ex-
pansion in the production of synthetics derived from benezenoid com-
pounds. Herbicides, insecticides and fungicides of this group have
been used in increasing quantities.

The absorption spectrum of benzene and its derivatives is generally
characterized by intense absorption in the 250 - 260 nm region of the
ultraviolet spectrum. The absorption weakens or falls off towards 300
nm. A necessary precondition for photochemical reaction is the absorp-
tion of light, so that the possibility of chemical reaction increases
rapidly as the wavelength of incident light is decreased.

A small proportion of the solar spectrum falls below 300 nm, but
although this radiation is low in intensity, this radiation is much
more energetic than higher wavelengths. Energy of radiation is in-
versely proportional to wavelength, therefore the shorter wavelengths
in the near to middle ultraviolet (320 - 280 nm) are photochemically
active. They possess sufficient energy to disrupt many linkages be-
tween atoms in molecules. Thus photochemical reactions induced by
light below 300 nm generally involve bond breaking or rearrangement.
Photochemical products may have altered toxicity, biological activity,
or capacity to undergo degradation by comparison with the parent sub-
stance.

Secondary processes may also be responsible for photochemical
alteration of molecules. The process of sensitized photolysis in-
volves absorption of light by a molecular species which does not re-
act, but this 'excited' species brings about reaction in a non-absorbing
species. The process of photosensitization may be common in the
environment, since natural waters contain unknown sensitizer molecules.
Rates of photodecomposition may often be greater in natural waters
than in distilled water. Reaction with oxygen under the action of
light or 'photooxidation' is also a common phenomenon responsible for
the degradation of many organic molecules.

Such phenomena alter the effectiveness of pesticide molecules. For example, the pyrethroids are particularly susceptible to photochemical breakdown, but a wide variety of molecules may be affected. Research into the area of pesticide photodecomposition has been carried out for a number of years. The information developed is of potential value in developing future strategies of pesticide use and maintaining pesticide efficacy.

Development of reliable information on the hazard and toxicology of photoproducts is limited by (i) the ignorance of their chemical nature, (ii) a lack of standardized procedures for investigation of photochemical reactions, (iii) a lack of information about the macro and micro environments to which pesticides are exposed in the field. This includes the intensity and distribution of solar energy, effects of adsorption on soil, dust, or foliar surfaces and the effects of sensitizers.

This information is needed if pesticides are to be used effectively, since residual activity may be considerably reduced by irradiation. Protecting agents and formulation techniques must be developed. Conventional pesticides have received some study and progress has been made in the pyrethroid field toward the solution of the problem by incorporation of new features in the molecule. Problems may also be encountered in the successful utilization of potential alternative pest control methods such as microbial agents, insect juvenile hormones, phenomones, chemosterilants, etc.

If chemicals are to be effectively used in agriculture, it is important that optimum conditions be defined for their effective use. Compounds which are potentially labile in sunlight must be identified. Methods of protection against sunlight should be sought and evaluated. Increased solar radiation on the earth's surface will result in increased photo-alteration of organic molecules. There should be an effort to estimate the quantitative significance of this increase in order to determine whether it will affect farm production and economics.

THE PHOTODEGRADATION OF AGRICULTURAL CHEMICALS AND RELATED ENVIRONMENTAL POLLUTANTS

The first year's work was planned as the basis of a continuing program in photochemistry. The most essential facilities of a photochemical laboratory were installed, and the physical and analytical techniques for the measurement of photochemical quantities were selected and tested. The accumulated experience from this phase of the program provides the background for its future expansion.

A number of pesticides, herbicides and related environmental pollutants were examined for suitability for study with the available apparatus in the B region of the ultraviolet spectrum. Finally, the set of nineteen chlorinated phenol isomers was chosen for the first large-scale comparison of a family of related compounds.

1) Apparatus for the Measurement of Quantum Yield

After a preliminary survey of the literature concerned with the measurement of quantum yield, it was decided to make initial determinations at 313 nanometers, because that is the only usable wavelength of the medium pressure mercury arc that falls within the B region of the ultraviolet.

A "merry-go-round" photolysis apparatus of the general type described by Moses, Liu and Monroe (1) was built. The support and drive mechanism were the standard components of the Ace Glass Company Model 6543 Turntable Photochemical Reactor. The sample holder and window system similar to that described by Moses was designed and constructed to our specifications. The aluminum parts were anodized black, and the apparatus was assembled and installed in a temperature-controlled water bath. To provide monochromatic radiation at 313 nanometers and to remove heat produced by the light source a cooled circulating filtering system was constructed (2).

2) Operation of the Photochemical Reactor

The photolysis apparatus was installed in the small inner room of a double darkroom. The power supply and controls were located in the outer darkroom. For safety, the power connection for the mercury arc was made through an electrical interlock on the door between them.

In tests with the filters covered by aluminum plates, no significant stray light was detected by ferrioxalate actinometer tubes in the sample holder.

The light intensity was found to increase by a large factor during a warm-up period. The extent to which this behavior depends upon the characteristics of the power supply was left for further investigation when time permits. For some of the earlier, shorter exposures, the problem was avoided by allowing a sufficient warm-up period, followed by a brief shutdown for sample insertion. For longer runs, the effect was not disturbing. The integrated light exposure, of course, depends upon the actinometer analysis, not upon the clock.

3) Actinometry

The potassium ferrioxalate actinometer was used as described in Murov's Handbook of Photochemistry (2). In that method, two separate solutions of ferric sulfate in sulfuric acid solution and of potassium oxalate are made up and standardized. The two solutions are stable indefinitely, and the actinometer is readily prepared by mixing and diluting them. Some recrystallized potassium ferrioxalate was also obtained for comparison. The extinction coefficient of the phenanthroline complex was determined for the available ultraviolet spectrophotometer, a Beckman DB-GT, by preparing a series of concentrations from a standardized ferrous sulfate solution, measuring the absorbances at 510 nm and applying a least squares treatment to the resulting data.

Although other workers have reported using very short exposures of ferrioxalate actinometers before and after long runs, the dependence of light intensity upon a warm-up period suggested using an actinometer capable of integrating light exposure throughout the longer photolysis times, which the dilute and sensitive ferrioxalate actinometer cannot do. The more concentrated uranyl oxalate actinometer was used, and the oxalate was titrated with potassium permanganate solution. Later, one of the organic ones, such as the malachite green leucocyanide actinometer, will be used.

4) The Selection of Compounds for Photolysis at 313 nm

Ultraviolet absorption spectra of a number of pesticides and herbicides were measured in water, ethanol and hexane solution, and a few candidates were selected for initial experiments. Pentachlorophenol was chosen for a study of the dependence of quantum yield on concentration. The choice of water as a solvent to simulate environmental conditions may, in some cases, require the use of concentrations lower than those usually used for quantum yield determinations. This problem has been discussed by R. G. Zepp et al. (3). The analytical problems suggest the use of compounds labeled with radioisotopes for counting or with stable isotopes for mass spectrometric multiple ion detection methods.

5) Analysis of Phenols

In order to permit the use of a chromatograph that could be conveniently obtained on loan, a method was developed for the determination by high

pressure liquid chromatography of phenols recovered from their aqueous
salt solutions by acidification and extraction. It has been used for
the sodium salts of chlorinated phenols.

6)   The Calculation of Quantum Yields

Each of the twenty tubes irradiated in the photochemical reactor
contained 4.00 ml of solution. Small losses of solvent by evaporation
need not be considered, because the entire contents of the tube were
quantitatively transferred for analysis. Because the volume was small,
it was often convenient to combine the contents of several tubes into
a single analytical sample. For example, ten tubes of uranyl oxalate,
in two groups of five, provided two identical samples for permanganate
titration, and ten tubes of pentachlorophenol sodium salt solution, in
two groups of five, could be processed to give two extracts for chroma-
tographic analysis. This technique need not result in any accumulation
of volumetric errors, since, where it is justified, the original 4.00-ml
aliquots can be dispensed from a buret in such a way that only the initial
buret reading for the first tube and the final buret reading for the last
tube are significant measurements for the group of tubes combined.

The oxalate in the uranyl oxalate actinometer was determined before
and after irradiation. The difference was used to calculate the number
of einsteins absorbed by a tube. Let n be a number of moles/tube or a
number of einsteins/tube, V be volume in liters (= 0.00400 liter/tube),
N be normality and M be molarity of solution. Let the subscripts I
denote initial values (before irradiation) and F denote final values
(after irradiation). The number of moles of oxalate ion destroyed per
tube is $\Delta n_{C_2O_4}=$ and the number of einsteins absorbed per tube is n_E.

$$\Delta n_{C_2O_4}^{=} \;=\; n_I - n_F$$

$$=\; V(M_I - M_F)$$

When the oxalate is titrated and calculated as oxalate ion concentration,

$$M = \frac{N}{2}$$

$$+ \frac{1}{2} \left[\frac{(V'_{KMnO_4} - blank) \times N_{KMnO_4}}{V'oxalate} \right].$$

V' is the volume of permanganate or combined oxalate sample in milliliters.
Since the quantum yield of the uranyl oxalate actinometer at 313 nm is
known (S. L. Murov, Handbook of Photochemistry) to be

$$0.561 = \frac{\Delta n_{C_2O_4}^{=}}{n_E},$$

we find that the number of einsteins absorbed per tube is

$$n_E = \frac{\Delta n_{C_2O_4}}{0.561} .$$

The number of einsteins absorbed per tube is the same for all tubes (actinometer and samples) because (1) the window size and shape are the same, (2) the radial distance from the lamp, the light distribution, etc., are averaged by the rotation and are therefore the same and (3) in this method of operation the absorbance of the solution in each tube is sufficient that essentially all of the acident light is absorbed.

If the volumes V" are chromatographic injection volumes in micro-liters, the molar concentrations of the PCP salt solutions before extraction are calculated as

$$M_{PCP} = M_{PCP, std.} \times \left[\frac{H_{PCP} \times \frac{V''_{PCP, std.}}{V''_{PCP}}}{H_{PCP, std.}} \right]$$

in which H is the chromatographic peak height in chart divisions, pro-vided that the volumes of the aqueous PCP sample and PCP standard solu-tion are equal, and that the volumes of the corresponding extracts are equal. The injected volumes are chosen to give approximately equal chromatographic peak heights, in order to avoid nonlinearity problems. The number of moles of PCP destroyed per tube if found by difference, as in the case of the actinometer. (Both the unirradiated and irradiated solutions are always extracted. The unirradiated one is the standard solution.)

$$\Delta n_{PCP} = n_I - n_F$$

Finally, the quantum yield for PCP disappearance at 313 nm is

$$\phi_{313} = \frac{\text{number of moles of PCP destroyed}}{\text{number of einsteins of light absorbed}}$$

$$\phi_{313} = \frac{\Delta n_{PCP}}{n_E} .$$

7)   The Quantum Yield as a Function of Concentration

The apparatus and techniques were first applied in the measurement of quantum yields for photodegradation by 313-nanometer radiation of

pentachlorophenol, present as the salt in aqueous sodium bicarbonate buffer solution (4). The extension of this experiment to lower concentrations could be done with isotopically labeled material, as noted above. Results for the higher concentrations of PCP are presented in Table 1.

Table 1. Quantum Yield for Degradation of Pentachlorophenol Sodium Salt

Starting Concentration of PCP	Irradiation Time in Hours	PCP Destroyed (%)	Radiation Intensity (E/tube/min)	Quantum Yield at 313 nm
0.000939M	2.00	28.0	9.1×10^{-7}	0.0096
0.000751	1.60	27.3	9.7×10^{-7}	0.0088
0.000751	0.80	8.8	9.1×10^{-7}	0.0061

In the first run for 2 hours, beginning with 0.000939M PCP of which 28.0% was destroyed, a quantum yield of 0.0096 was measured. In the second run, beginning with 0.000751M PCP, the time was reduced to 1.60 hours, to give about the same depletion of the PCP (27.3%), as expected. The quantum yield was a little smaller, 0.0088. In the third run, the time was reduced to 0.80 hour. The 0.000751M initial concentration was reduced by 8.8% by photolysis, with a quantum yield of 0.0061.

8)   Photodegradation of the Chlorinated Phenol Isomers

As the concluding step in the initial program, a comparative study of the quantum yields for photodegradation of the complete set of nineteen chlorinated phenol isomers has been begun. Some of them are important as environmental pollutants (5). The scheduled completion of this phase was interrupted by problems. The first was unavailabity of analytical assistance at the most critical point. The second was the inadequacy of the laboratory ventilation system to remove volatile irritants in some of the runs. As a general safety measure, the photolysis apparatus is being moved into an available small fume hood. Therefore the examination of this set of compounds has been suspended until after the reinstallation of the apparatus.

References

(1)   F. Guy Moses, Robert S. H. Liu and Bruce M. Monroe, Molecular Photochemistry 1, 245-249 (1969).

(2)   Steven L. Murov, Handbook of Photochemistry, Marcel Dekker, New York, 1973.

(3)   R. G. Zepp,   Unpublished work.

(4)   C. W. Hiatt, W. T. Haskins and L. Olivier, The American Journal of Tropical Medicine and Hygiene 9, 527-531 (1960).

(5)   Akio Yasuhara, Akira Otsuki and Keiichiro Fuwa, Chemosphere 6, 659-664 (1977).

Figure 1.   The Parts of the Anodized Aluminum Sample Holder-Window System
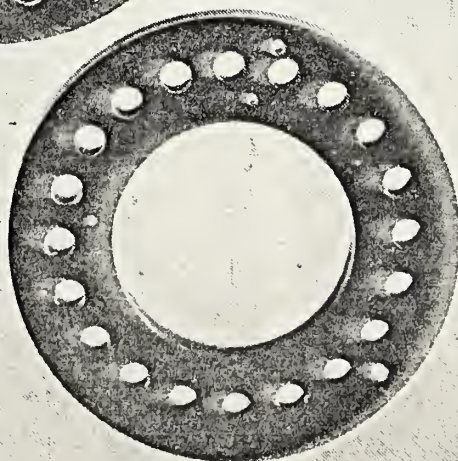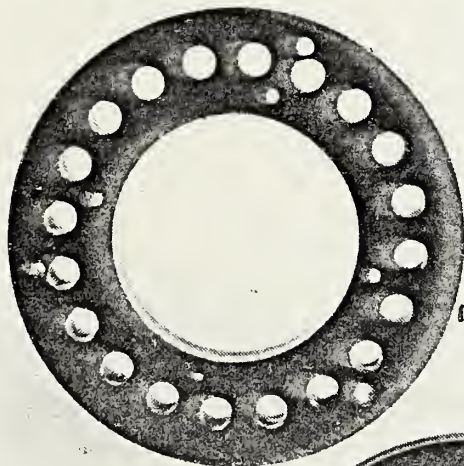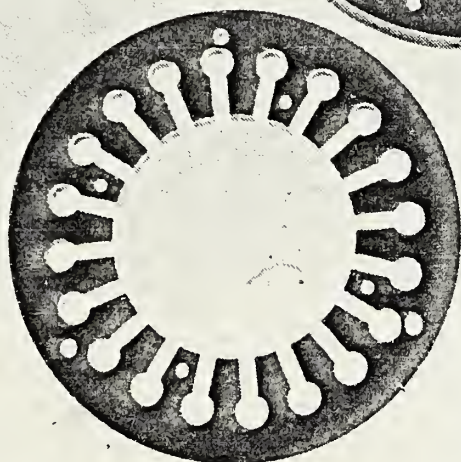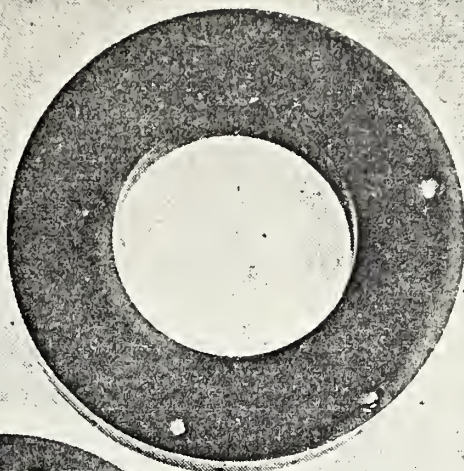
Figure 2. The Sample Holder-Window System
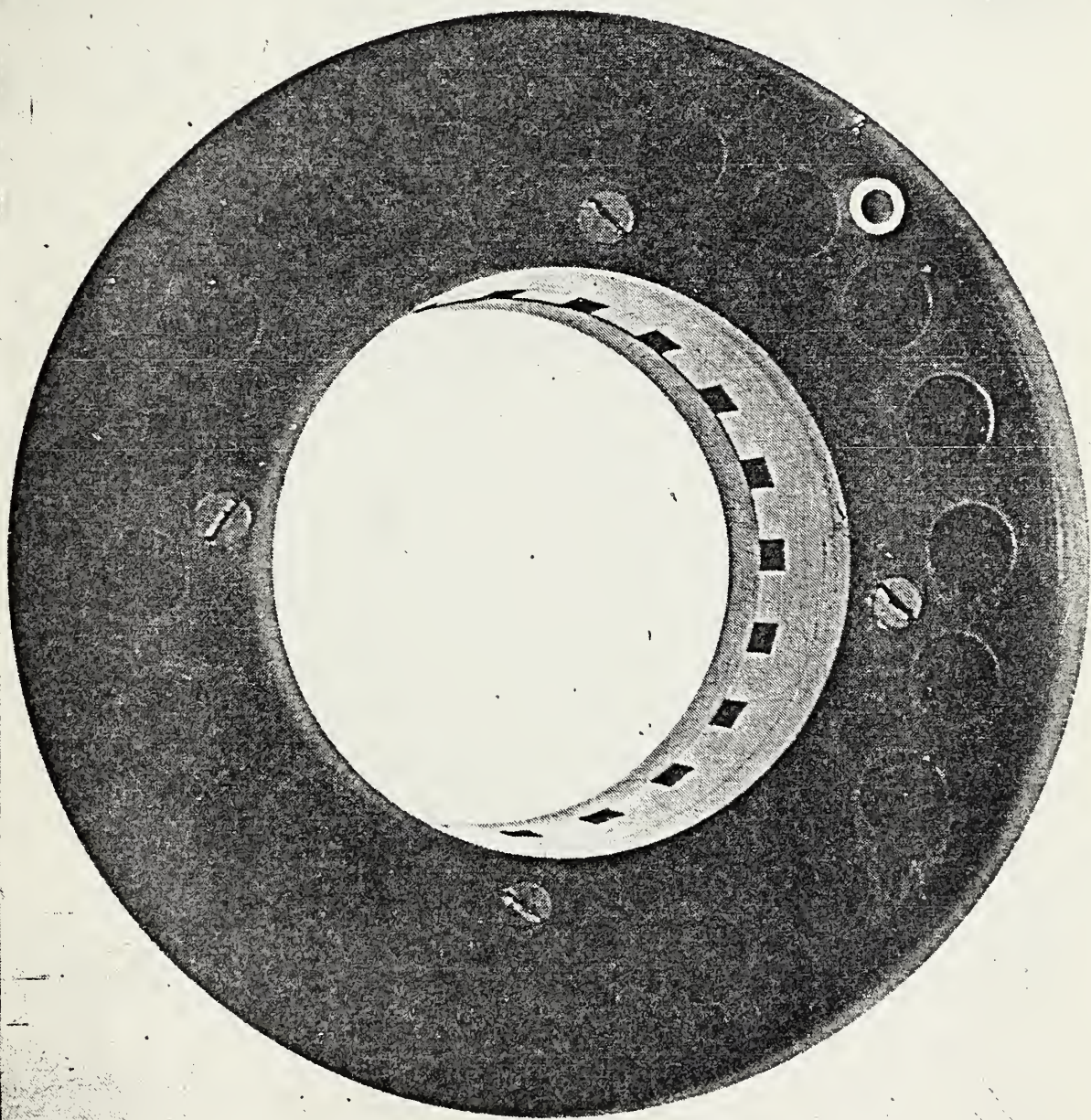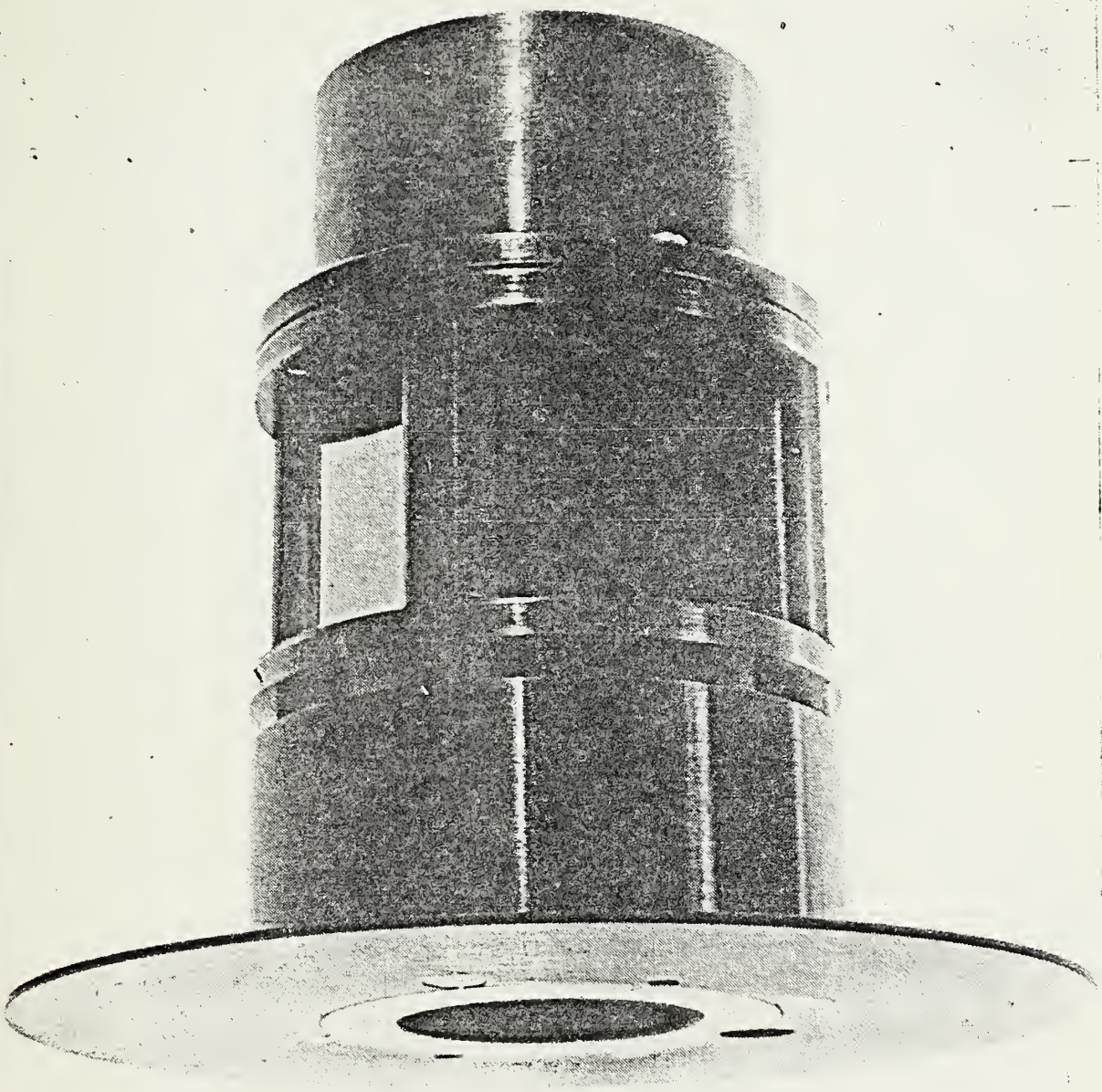
Figure 3. The Filter Holder and Attached Light Shields
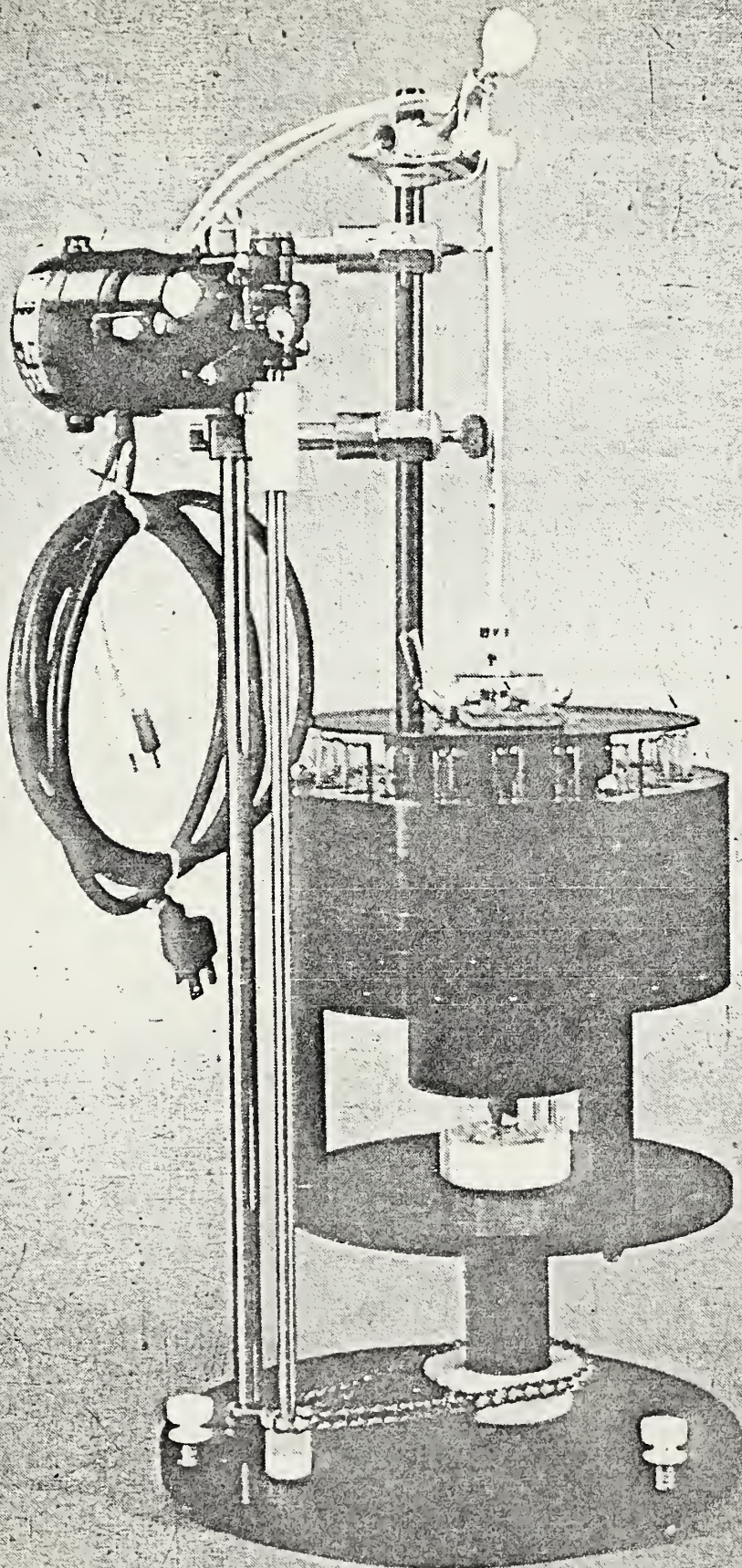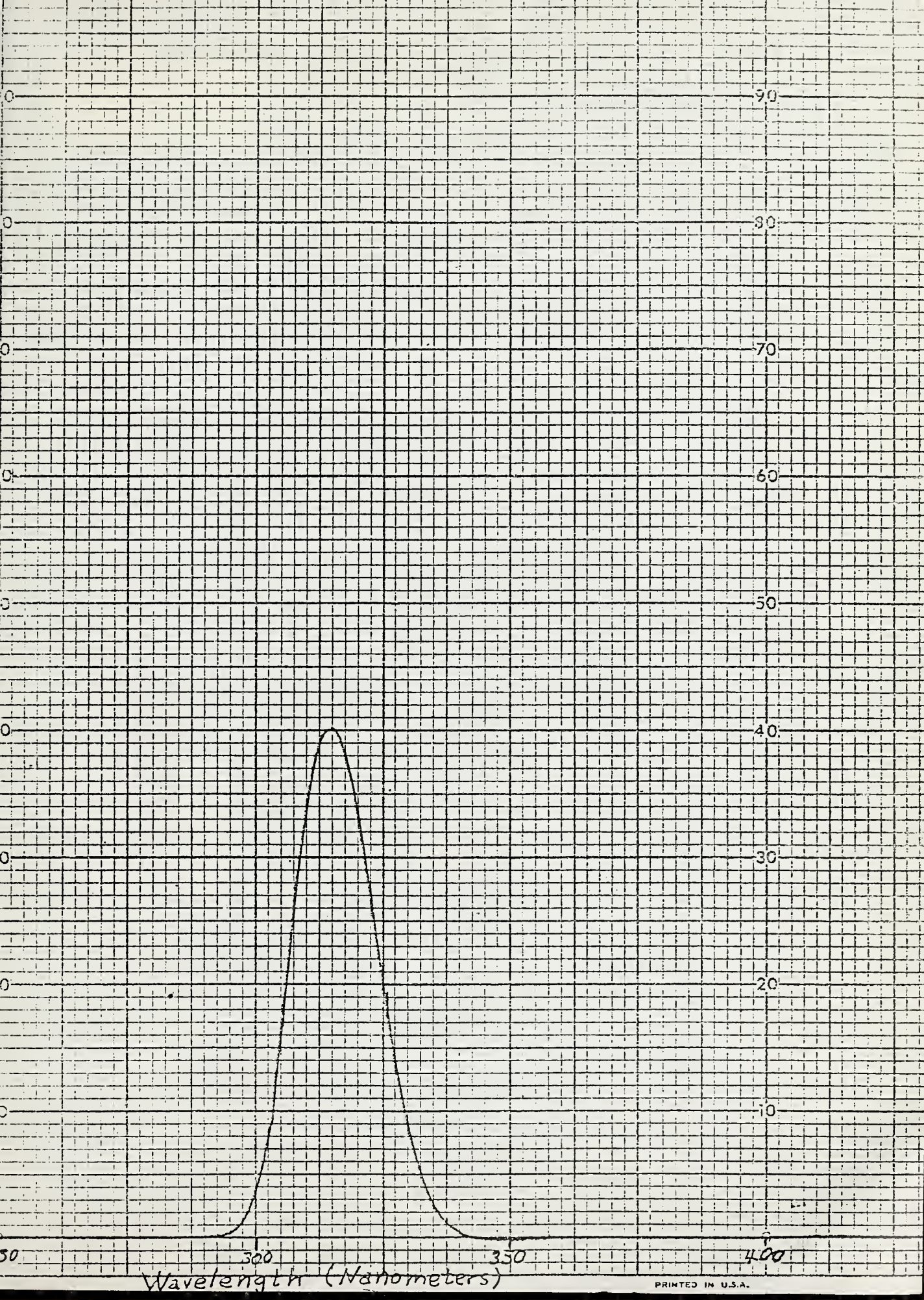
Figure 4.   The "Merry-Go-Round" Photochemical Reactor

Figure 5.   The Transmittance Spectrum of the Combined Filter for
the 313-Nanometer Mercury Line

Wavelength (Nanometers)